PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference Q036334PPC	**FOR FURTHER ACTION** see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/GB 98/ 02082	International filing date *(day/month/year)* 15/07/1998	(Earliest) Priority Date *(day/month/year)* 19/07/1997
Applicant THE UNIVERSITY OF BIRMINGHAM et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. [ ] **Certain claims were found unsearchable** (see Box I).

2. [ ] **Unity of invention is lacking** (see Box II).

3. [ ] The international application contains disclosure of a **nucleotide and/or amino acid sequence listing** and the international search was carried out on the basis of the sequence listing
   - [ ] filed with the international application.
   - [ ] furnished by the applicant separately from the international application,
     - [ ] but not accompanied by a statement to the effect that it did not include matter going beyond the disclosure in the international application as filed.
   - [ ] Transcribed by this Authority

4. With regard to the **title**,
   - [X] the text is approved as submitted by the applicant
   - [ ] the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,
   - [X] the text is approved as submitted by the applicant
   - [ ] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this International Search Report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is:

   Figure No. 1
   - [X] as suggested by the applicant.
   - [ ] because the applicant failed to suggest a figure.
   - [ ] because this figure better characterizes the invention.
   - [ ] None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 98/02082

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C23C8/10 C23C8/80

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	A. TAKAMURA: "surface hardening of titanium by oxygen" TRANS JIM, vol. 3, 1962, pages 10-14, XP002080647 cited in the application	1,3
A	see page 10 - page 14	11,12
Y	PATENT ABSTRACTS OF JAPAN vol. 015, no. 167 (C-0827), 26 April 1991 & JP 03 036256 A (MITSUBISHI MOTORS CORP), 15 February 1991 see abstract	1,3
A	PATENT ABSTRACTS OF JAPAN vol. 011, no. 043 (C-402), 7 February 1987 & JP 61 207568 A (NIPPON STEEL CORP), 13 September 1986 see abstract	1

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 October 1998	27/10/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Elsen, D

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 98/02082

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 016, no. 128 (C-0924), 2 April 1992 & JP 03 294471 A (KOBE STEEL LTD), 25 December 1991 see abstract	1
A	CASIMIR J. ROSA: "the oxidation of zirconium in oxygen-nitrogen atmospheres" ZEITSCHRIFT FUR METALLKUNDE, vol. 71, no. 7, July 1980, pages 470-474, XP002080648 stuttgart,de see page 470 - page 474	1,3,4
A	US 5 588 443 A (JAMES A. DAVIDSON) 31 December 1996 see column 10, line 31 - line 64; claims 1,3,4	1
A	EP 0 244 253 A (HONDA MOTOR) 4 November 1987 see claim 9	1
A	WO 96 23908 A (SMITH & NEPHEW RICHARDS) 8 August 1996 see page 11, line 1 - page 14, line 3	1

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 98/02082

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5588443 A	31-12-1996	US 5496359 A	05-03-1996
		US 5282850 A	01-02-1994
		US 5258022 A	02-11-1993
		US 5152794 A	06-10-1992
		US 5037438 A	06-08-1991
		US 5549667 A	27-08-1996
		US 5632779 A	27-05-1997
		US 5611347 A	18-03-1997
		US 5647858 A	15-07-1997
		US 5649951 A	22-07-1997
		US 5628790 A	13-05-1997
		AU 675450 B	06-02-1997
		AU 4786293 A	14-02-1994
		CA 2141183 A	03-02-1994
		EP 0746266 A	11-12-1996
		JP 8501953 T	05-03-1996
		WO 9402083 A	03-02-1994
		AU 660893 B	06-07-1995
		AU 3217593 A	05-08-1993
		CA 2088696 A	05-08-1993
		EP 0555038 A	11-08-1993
		AU 639468 B	29-07-1993
		AU 5980790 A	31-01-1991
		DE 69005219 D	27-01-1994
		DK 410711 T	11-04-1994
		EP 0410711 A	30-01-1991
		ES 2048435 T	16-03-1994
		JP 4144555 A	19-05-1992
		CA 2021814 A	26-01-1991
		US 5370694 A	06-12-1994
		US 5180394 A	19-01-1993
EP 244253 A	04-11-1987	JP 62256956 A	09-11-1987
WO 9623908 A	08-08-1996	AU 5295396 A	21-08-1996
		ZA 9600541 A	14-08-1996

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PATENT COOPERATION TREATY

REC'D 2 8 APR 1999

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference QO36334PPC	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/GB98/02082	International filing date *(day/month/year)* 15/07/1998	Priority date *(day/month/year)* 19/07/1997
International Patent Classification (IPC) or national classification and IPC C23C8/10		
Applicant THE UNIVERSITY OF BIRMINGHAM et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 6 sheets, including this cover sheet.

   ☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of sheets.

3. This report contains indications relating to the following items:

   I ☒ Basis of the report
   II ☐ Priority
   III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   IV ☐ Lack of unity of invention
   V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   VI ☐ Certain documents cited
   VII ☐ Certain defects in the international application
   VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
08/02/1999	26.04.99
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. (+49-89) 2399-0 Tx: 523656 epmu d Fax: (+49-89) 2399-4465	Authorized officer Hahn, H Telephone No. (+49-89) 2399

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-11 as originally filed

Claims, No.:

1-19 as originally filed

Drawings, sheets:

1/4-4/4 as originally filed

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB98/02082

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-19
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-19
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-19
	No:	Claims	

2. Citations and explanations

see separate sheet

INTERNATIONAL PRELIMINARY EXAMINATION REPORT - SEPARATE SHEET

International application No. PCT/GB98/02082

1. Section V:

The documents of the International Search Report are regarded to be relevant as follows:

D1 = A. TAKAMURA: "surface hardening of titanium by oxygen" TRANS JIM, vol. 3, 1962, pages 10-14 (cited in the application)
D2 = PATENT ABSTRACTS OF JAPAN vol. 015, no. 167 (C-0827), 26 April 1991 & JP-A-03 036 256
D3 = PATENT ABSTRACTS OF JAPAN vol. 011, no. 043 (C-402), 7 February 1987 & JP-A-61 207 568
D4 = PATENT ABSTRACTS OF JAPAN vol. 016, no. 128 (C-0924), 2 April 1992 & JP-A-03 294 471
D5 = CASIMIR J. ROSA: "the oxidation of zirconium in oxygen-nitrogen atmospheres" ZEITSCHRIFT FUR METALLKUNDE, vol. 71, no. 7, July 1980, pages 470-474
D6 = US-A-5 588 443
D7 = EP-A-0 244 253
D8 = WO-A-9 623 908

1.1 The claims 16-19 of this application are interpreted as product claims 'per se'. Therefore any document which discloses such a claimed product - even if obtained by a different process - takes away the novelty of the claimed subject-matter.

1.2 Document D1 discloses results of surface hardening of Ti-metal by oxygen. Two processes were tested, the first one used dry oxygen for oxidation of the Ti at 850°C with a subsequent diffusion treatment for 0-48 hours in an Ar atmosphere, the second process utilized a direct diffusion of oxygen in a molten glass bath at a temperature of 850°C (cf. pages 10-11, abstract and paragraph II, experimental procedure). D1 further states that heating Ti in air or an oxygen atmosphere results in the formation of a considerable amount of scale which roughens the surface and causes serious embrittlement (cf. page 10, left column, penultimate paragraph to right column).

The use of a mixture of nitrogen and oxygen, particularly air is thus neither disclosed nor suggested. Also a sigmoid-shaped hardness profile is neither disclosed nor suggested. To the contrary, the hardness profile disclosed in D1 (cf. figures 2-3 and 5-

7) corresponds to that shown in figure 2 of the application for the mere oxidation treatments (cf. figure 2). Hence D1 cannot give the skilled person any incentive to derive such a sigmoid-shaped hardness profile, let alone when starting from the described processes. Hence D1 cannot be combined with document D2 - which discloses the use of a mixture of nitrogen and oxygen - in an obvious manner. The same conclusion applies to any of the other documents D2-D8.

1.3 Document D2 discloses the use of a mixture of nitrogen and oxygen for treating Ti and Ti alloys in order to obtain a desired hardness (cf. abstract). However, D2 does neither disclose a subsequent heat treatment nor a sigmoid-shaped hardness profile. Hence D2 is considered not to be particularly relevant. The skilled person has no conclusive reason at all (no specific improvement or effect is to be expected) to combine the documents D1 and D2 which use different oxidation atmospheres.

1.4 Document D3 discloses another surface treatment of Ti or Ti alloys wherein the oxidized Ti article is heat treated in vacuum or in an inert gas atmosphere at or above 700°C (cf. abstract). D3 does not specify any treatment parameters such as to how the oxide layer was produced. Furthermore, no sigmoid-shaped hardness profile mentioned or suggested. Hence D3 is also not particularly relevant.

1.5 Document D4 discloses an oxidative film on a Ti sheet preferably obtained by anodization during the degreasing of said sheet which is then diffused into the surface layer by annealing the said sheet (cf. abstract). No oxidation in a nitrogen/oxygen containing atmosphere disclosed. Also no sigmoid-shaped hardness profile mentioned (which is not the direct result of annealing an oxidized surface layer). Hence D4 is also not considered to be particularly relevant.

1.6 Document D5 discloses investigation results of the oxidation of Zr in oxygen-nitrogen atmospheres (cf. abstract; experimentals). There is no subsequent annealing treatment disclosed or suggested as well as no sigmoid-shaped hardness profile. Hence D5 is not relevant at all.

1.7 Document D6 discloses the production of Zr articles having a blue to black zirconium oxide or nitride coating (cf. abstract; examples). No subsequent heat treatment disclosed or suggested as well as no sigmoid-shaped hardness profile.

Hence D6 is not relevant.

1.8 Document D7 discloses a surface treatment of Ti articles by direct oxidation thereof using a longer treatment of 3-5 hours (cf. examples; claims) in air atmosphere but without subsequent heat treatment, let alone in the required atmosphere and temperature conditions. Hence D7 is also not relevant.

1.9 Document D8 discloses a wear resistant tribosystem based on Ti articles containing an amount of Zr obtained in an oxygen-containing (but different because argon-oxygen-water vapour) atmosphere at temperatures between 200-700°C (according to the examples generally at 500°C) for about 2.5 hours and a heat treatment in the same atmosphere (cf. examples; claims). Hence totally different process parameters and - consequently - no resulting sigmoid-shaped hardness profile disclosed or suggested. Therefore D8 is also not considered to be relevant.

1.10 As a consequence of the paragraphs 1.1 to 1.9 above the claims 1-19 meet the requirements of Articles 33(2) and (3) PCT. The industrial applicability of the claimed case hardening process and the claimed case hardened products having the sigmoid-shaped hardness profile is self-evident.

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C23C 8/10, 8/80

A1

(11) International Publication Number: WO 99/04055

(43) International Publication Date: 28 January 1999 (28.01.99)

(21) International Application Number: PCT/GB98/02082

(22) International Filing Date: 15 July 1998 (15.07.98)

(30) Priority Data:
9715175.7 19 July 1997 (19.07.97) GB

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(72) Inventors; and
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(74) Agents: PEARCE, Anthony, Richmond et al.; Marks & Clerk, Alpha Tower, Suffolk Street Queensway, Birmingham B1 1TT (GB).

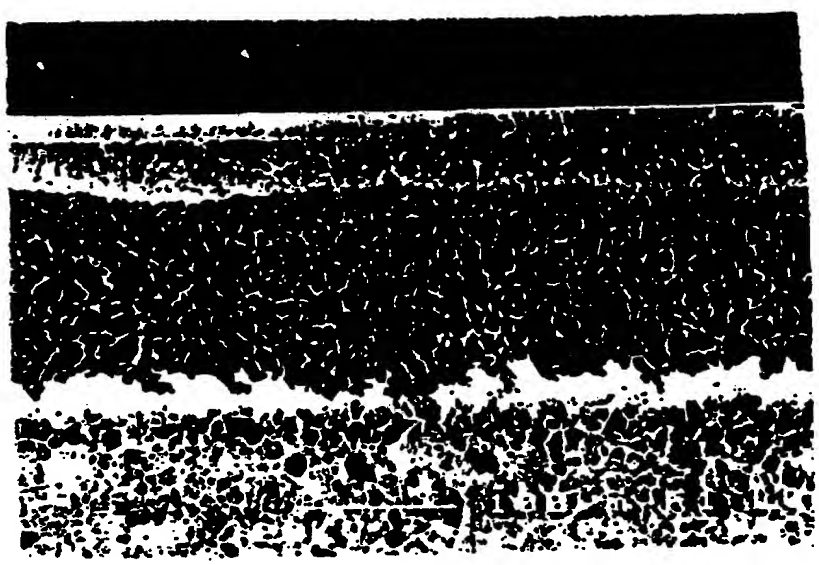
(81) Designated States: CA, JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: METHOD OF CASE HARDENING

(57) Abstract

A method of case hardening an article formed of titanium, zirconium or an alloy of titanium and/or zirconium is disclosed. First, the article is heat–treated in an oxidising atmosphere at a temperature in the range of 700 to 1000 °C so as to form an oxide layer on the article. Then, the article is further heat–treated in a vacuum or in a neutral or inert atmosphere at a temperature in the range of 700 to 1000 °C so as to cause oxygen from the oxide layer to diffuse into the article.



METHOD OF CASE HARDENING

This invention relates to a method of case hardening and is more particularly concerned with a method of case hardening an article formed of titanium, zirconium or an alloy of titanium and/or zirconium.

In engineering applications, when a surface is subjected to a high contact load by another body, internal stresses are developed below the surface, the so-called Hertzian stresses. These stresses reach a maximum at a certain depth below the surface. Consequently, in order to withstand such stresses, it is necessary for a case-hardened layer to provide increased strength (and therefore hardness) down to at least that depth. At the same time, it is desirable to avoid excessive hardness at the surface itself as this could cause embrittlement. To reconcile these requirements, it is generally preferred to produce a hardness profile, in the direction normal to the surface, which has a sigmoid shape (see, for example, the OD curve in accompanying Fig 2), consisting of a region of relatively high hardness maintained to a certain depth below the surface before dropping more steeply and then gradually to the hardness of the untreated core material.

Both theoretical and experimental work has shown that significant improvements in the load-bearing capacity of a hard coating/sub structure system can be achieved provided that, in addition to a high interfacial adhesion strength, the substrate can firmly withstand the applied load without appreciable plastic deformation. This means that deep case surface engineering processes are beneficial for subsequent hard thin coatings on titanium alloys in view of their inherent low yield strengths and low elastic moduli. However, most titanium alloys, unlike ferrous materials, cannot be hardened to a great extent by conventional surface engineering techniques since there is no hardening reaction in titanium

alloys comparable to the martensite transformation in ferrous materials. Notwithstanding the fact that titanium alloys can be deeply hardened by electron beam surface alloying, it is still difficult in practice to achieve controlled reproducibility of composition in the alloyed surface layer. Oxidising titanium alloys at a high oxidation temperature for an extended period of time can also produce a deep hardened case. However, simple oxidation at higher temperatures (greater than 700°C) is prone to the formation of severe scaling, resulting in a crumbly surface oxide layer. The present invention relates to a method which avoids this by oxidation treatment at an elevated temperature effected for a relatively short period of time, followed by a subsequent heat treatment operation.

A method of surface hardening titanium by oxygen is disclosed by A. Takamura (Trans JIM, 1962, Vol. 3, pages 10-14). In one of the methods disclosed by Takamura, samples of commercial titanium are annealed, polished and degreased and are then oxidised in dry oxygen at 850°C for 1 or 1.5 hours. A thin oxide scale is formed on the surface of the samples. Then, the thus-oxidised samples are subjected to a diffusion treatment at 850°C for 24 hours in argon so as to cause oxygen to diffuse into the sample. In other methods disclosed by Takamura, the oxidised samples are diffusion treated first in argon and then in nitrogen or are diffusion treated in nitrogen. In no case, however, is the desirable sigmoid-shaped hardness profile achieved.

It is an object of the present invention to provide a process which is more capable of achieving the desirable sigmoid-shaped hardness profile than the last-mentioned publication.

According to a first aspect of the present invention, there is provided a method of case hardening an article formed of titanium, zirconium or an

alloy of titanium and/or zirconium, said method comprising the steps of (a) heat-treating the article formed of titanium, zirconium or alloy of titanium and/or zirconium in an oxidising atmosphere containing both oxygen and nitrogen at a temperature in the range of 700 to 1000°C so as to form an oxide layer on the article; and (b) further heat-treating the article in a vacuum or in a neutral or an inert atmosphere at a temperature in the range of 700 to 1000°C so as to cause oxygen from the oxide layer to diffuse into the article.

According to a second aspect of the present invention, there is provided a method of case hardening an article formed of titanium, zirconium or an alloy of titanium and/or zirconium, said method comprising the steps of (a) heat-treating the article formed of titanium, zirconium or alloy of titanium and/or zirconium in an oxidising atmosphere at a temperature in the range of 700 to 1000 °C so as to form an oxide layer on the article; and (b) further heat-treating the article in a vacuum or in a neutral or an inert atmosphere at a temperature in the range of 700 to 1000°C so as to cause oxygen from the oxide layer to diffuse into the article whereby to produce a sigmoid-shaped hardness profile.

The time for heat-treatment in step (a) is relatively short and depends, inter alia, upon the nature of the oxidising medium and the intended use of the article. Typically, the time may be, for example, from 0.1 to 1 hour, preferably 0.3 to 0.6 hour.

The heat-treatment in step (a) is conveniently effected at atmospheric pressure.

Steps (a) and (b) may be repeated at least once.

In the method according to said second aspect of the present invention, the oxidising atmosphere in step (a) preferably comprises oxygen as well as nitrogen, as this improves the adhesion of the predominantly oxide scale thus formed.

In the first and second aspects of the present invention, the oxidising atmosphere in step (a) is preferably air. The temperature in step (a) is preferably 700 to 900 °C, more preferably 800 to 900 °C, and most preferably about 850 °C.

The temperature in step (b) is preferably 700 to 900 °C, more preferably about 800 to 900 °C, and most preferably about 850 °C. It is most preferred to effect treatment step (b) in a vacuum, in which case the pressure is preferably not more than 1.3 x 10^{-2} Pa (1 x 10^{-4} Torr) Pa, and is conveniently about 1.3 x 10^{-4} Pa (1 x 10^{-6} Torr). The use of a vacuum is much preferred because it reduces the risk of unwanted contaminants being accidently introduced into the surface of the article during step (b).

In particular, it is important to prevent gaseous oxygen from reaching the solid surface during step (b) where it may dissolve or react so as to cause excessive hardness and potential embrittlement. Where the heat treatment in step (b) is effected in an inert or neutral atmosphere, any non-oxidising and non-reducing atmosphere may be employed, such as argon or other inert gas, provided that it contains no or only a low partial pressure of oxygen.

The time required for the heat treatment in step (b) is typically in the range of 10 to 50 hours and may conveniently be about 20 to 30 hours.

It is within the scope of the present invention to follow the treatment steps

(a) and (b) with any of a variety of subsequent treatments or processes to reduce friction. In particular, it is within the scope of the present invention to follow the method of the present invention with the treatment method disclosed in our copending PCT Publication No. WO98/02595 for improving the tribological behaviour of a titanium or titanium alloy article. Such process basically involves the gaseous oxidation of the article at a temperature in the range of 500 to 725 °C for 0.5 to 100 hours, the temperature and time being selected such as to produce an adherent and essentially pore-free surface compound layer containing at least 50 % by weight of oxides of titanium having a rutile structure and thickness of 0.2 to 2 μm on a solid solution - strengthened diffusion zone where the diffusing element is oxygen and the diffusion zone has a depth of 5 to 50 μm.

The present invention is applicable to commercially pure grades of titanium, titanium alloys (α,$\alpha+\beta$, or β alloys), commercially pure grades of zirconium, zirconium alloys and to alloys of zirconium and titanium.

Where the article is required to have good fatigue properties, it may be subjected to a mechanical surface treatment, such as shot peening, after heat treatment in order to restore the fatigue properties which may be reduced by the heat treatment operation.

According to a third aspect of the present invention, there is provided an article formed of a metal or alloy selected from titanium, zirconium, alloys of titanium and alloys of zirconium, said article having a hardened metallic case, strengthened by diffused oxygen; wherein the article has a sigmoid-shaped hardness profile across said hardened case.

Preferably, the depth of the hardened case is greater than 50 μm, and is

typically in the range 200 to 500 μm, but may be as great as 1 mm.

A further layer of low-friction material, for example, a nitride, diamond-like-carbon or an oxide layer as described in our co-pending PCT Publication No. WO98/02595, may be provided on top of the hardened case.

In the accompanying drawings:-

Fig 1 is an SEM micrograph showing the overall microstructure of a sample of an oxygen-diffused (OD) Ti6Al4V material treated in accordance with the method of the present invention,

Fig 2 is a graph showing microhardness profiles for the OD Ti6Al4V material produced in accordance with the present invention and for other surface-treated articles formed of the same material (Ti6Al4V),

Fig 3 is a graph showing the effect of OD treatment and OD plus shot peening (OD+SP) on the fatigue properties of Ti6Al4V,

Fig. 4 is a graph showing microhardness profiles for OD C.P titanium material, produced in accordance with the present invention,

Fig. 5 is a graph showing a microhardness profile for OD Timet551 produced in accordance with the present invention, and

Fig. 6 is a graph showing a microhardness profile for OD Timet10-2-3 material, produced in accordance with the present invention.

Samples of Ti6Al4V in the form of cylindrical coupons of 5 mm thickness, cut from a 25 mm diameter bar were used. The samples were then thoroughly cleaned and subsequently thermally oxidised at 850 °C for 30 minutes in air in a muffle furnace. After being allowed to cool, the samples were subjected to a further heat treatment operation at 850 °C for 20 hours in a vacuum furnace (about 1.3×10^{-4} Pa = about 10^{-6} Torr). Alternatively, the steps of (a) thermal oxidation and (b) further heat

treatment can be carried out in a single vacuum furnace, step (a) being effected in air and step (b) being effected at 1.3 x 10^{-4} Pa after evacuation of the air.

It was noted that, after thermal oxidation at 850 °C for 30 minutes, the samples had a dark brown appearance. However, this changed to silver following the further heat treatment operation. The metallography of the oxygen-diffused treated sample is shown in Fig 1. A hardened layer was produced which was which was estimated from the transition in morphology to have a depth of about 300 µm and appeared (from the different etching effects) to consist of two sub-layers, the first sub-layer having a depth of about 80µm and the second sub-layer, lying under the first sub-layer, having a depth of about 220 µm.

A typical microhardness profile for the above-treated samples is illustrated in Fig 2 where, for comparison purposes, microhardness profiles are also given for samples of the same Ti6Al4V material treated by one of three processes, namely oxidation at 850 °C for 30 minutes, oxidation at 850°C for 20.5 hours and plasma nitriding at 850°C for 20 hours in an atmosphere of 25% N_2 and 75% H_2. It is notable that the OD material treated in accordance with the present invention showed the desired sigmoid hardness profile with a more pronounced hardening effect in terms of higher hardness and deep-hardened zone than the thermally oxidised material with the same thermal cycle (850 °C/20.5 hours). The microhardness profile for the OD material in accordance with the present invention is in good agreement with the observed microstructural features illustrated in Fig 1.

As can be seen from Fig 2, the OD samples produced in accordance with the present invention had a high hardness (greater than 700 $HV_{0.05}$) in the

first 80 μm and a total hardened layer of about 300 μm in depth.

As can be seen from Fig 3, OD treatment in accordance with the present invention reduces the fatigue properties of Ti6Al4V. However, the reduction in the fatigue limit was totally restored and slightly elevated by about 30 MPa over the untreated material by shot peening. In this particular case, the shot peening was effected using C glass shot with an Almen density of 0.15-0.029N.

As noted above, the samples treated in accordance with the present invention possessed a significantly greater depth of hardening effect than a direct oxidation treatment at the same temperature and for the same total time (850 °C/20.5 hours). This means that the treatment in accordance with the present invention not only avoids the formation of an undesirable scale, which always occurs as a result of oxidation treatment at high temperature, but also confers a greater case hardening effect. This phenomenon at first seems difficult to understand since, in both instances, a high oxygen potential exists at the air/oxide interface for the oxidation treatment or at the oxide/Ti interface for the treatment in accordance with the present invention. It is known that oxidation of titanium is controlled by oxygen diffusion in the diffusion zone rather than in the oxide, since the diffusion coefficient for oxygen in TiO_2 is about 50 times that in α-Ti at the same temperature. Therefore, there is no reason to relate to the difference in the hardening effect between the process of the present invention conducted at 850 °C for a total time of 20.5 hours and a simple oxidation treatment effected at 850 °C for 20.5 hours, to the diffusion resistance of oxygen passing through the oxide layer.

Without prejudice to the present invention, it is theorised that the above phenomenon is caused by the retarding effect of nitrogen (from the air) on

the diffusion of oxygen. During prolonged treatment in air, a build-up of nitrogen atoms may occur at the oxide/metal interface (see A.M. Chaze et al, Journal of Less-Common Metals, 124 (1986) pages 73 to 84) and may act as a block on the inward diffusion of oxygen. In the above described process according to the present invention, no further nitrogen is admitted during vacuum treatment and the blocking effect is therefore much reduced.

The examples quoted above for the alloy Ti-6A1-4V, have been case hardened using process parameters that have substantially been optimised for that alloy. In order to demonstrate that the process is equally applicable to other alloys of titanium, a limited number of samples of C.P titanium, Timet551 and Timet10-2-3 have also been treated. The following examples are for demonstration only and do not necessarily represent an optimised process.

Samples of C.P titanium in the form of rectangular blocks of 20x10x10mm, cut from a 10mm thick sheet, were used. The samples were degreased and then thermally oxidised in air at 850 °C for 20-30 minutes. After cooling, the samples were subjected to a further heat treatment operation at 850 °C for 22 hours in a vacuum furnace (about 1×10^{-6} Torr = about 1.3×10^{-4} Pa).

Samples of Timet551 in the form of rectangular blocks of 30x10x10mm, cut from a 90mm diameter bar, were used. The samples were degreased and then thermally oxidised in air at 900 °C for 19 minutes. After cooling, the samples were subjected to a further heat treatment operation at 900 °C for 20 hours in a vacuum furnace (about 1×10^{-6} Torr = about 1.3×10^{-4} Pa).

Samples of Timet10-2-3 in the form of rectangular blocks of 30x10x10mm,

cut from a 260 mm diameter forged disc, were used. The samples were degreased and then thermally oxidised in air at 900 °C for 25 minutes. After cooling, the samples were subjected to a further heat treatment operation at 900 °C for 20 hours in a vacuum furnace (about $1x10^{-6}$Torr=about $1.3x10^{-4}$Pa).

It was noted that, after thermal oxidation, the C.P and Timet551 samples exhibited a grey appearance, whereas the Timet10-2-3 material exhibited a black appearance.

As can be seen from Figs 4 and 5, the C.P and Timet551 hardness profiles exhibit the same type of sigmoid shape as Fig. 2 (OD) but 20 μm deeper penetration in the case of Timet551 (c.f. Fig. 2); the slightly lower hardness and deeper penetration being attributed to the 20 hour 900 °C diffusion step.

As can be seen from Fig. 6, the metastable β material has developed a much deeper hardening compared with the $\alpha+\beta$ titanium alloys. The deeper penetration of the oxygen can firstly be attributed to the higher diffusivity of oxygen in the β phase (see Z. Liu and Welsch, Metallurgical Trans. A, Vol. 19A, April 1988, pg1121-1125) and also to a much thicker oxide layer which developed during step (a), compared with the $\alpha+\beta$ titanium alloys.

In some alloys, the thermochemical treatment carried out in step (a) and/or step (b) of the case hardening process may alter the microstructure and mechanical properties of the core material. In such cases, a further heat treatment may be carried out after the case hardening process in order to restore or optimise the core properties.

It is important in the present invention that the scale formed during step (a) should remain adherent to the surface in order to provide the oxygen reservoir required for step (b). Depending on the alloy, the adhesion of the scale during step (a) can be affected not only by the time and temperature employed but also by the nature of the oxidising atmosphere and by the surface finish and geometrical shape of the surface treated. When titanium is oxidised at around 850°C, the scale formed is significantly more adherent if the oxidising atmosphere is air rather than pure oxygen, and a model has been proposed to explain this as an effect of the presence of nitrogen. Our experiments have confirmed the superiority of an air atmosphere over oxygen in this respect, and it is therefore not only more economical but also a technically preferred option to use air as the oxidising atmosphere in step (a). The surface finish applied to all samples here described was obtained by finishing on 1200 grade SiC paper and this generally gave good adhesion.

It is to be understood that the case hardening process here described results in a relatively deep case of hardened material which enables it to withstand the sub-surface Hertzian stresses developed by high contact loads. The resultant surface has therefore a high load-bearing capacity, but this does not, of itself, confer good wear resistance to the surface. In order to obtain a surface with low friction, which is resistant to scuffing and galling, it will be necessary to apply a further layer or coating to the case hardened surface, or other surface treatment. Coatings, which have successfully been applied to the case hardened surface, include plasma nitriding, a diamond-like carbon coating, and the coating produced by the process described in our copending PCT Publication WO98/02595.

CLAIMS

1. A method of case hardening an article formed of titanium, zirconium or an alloy of titanium and/or zirconium, said method comprising the steps of (a) heat-treating the article formed of titanium, zirconium or alloy of titanium and/or zirconium in an oxidising atmosphere containing both oxygen and nitrogen at a temperature in the range of 700 to 1000 °C so as to form an oxide layer on the article; and (b) further heat-treating the article in a vacuum or in a neutral or an inert atmosphere at a temperature in the range of 700 to 1000 °C so as to cause oxygen from the oxide layer to diffuse into the article.

2. A method of case hardening an article formed of titanium, zirconium or an alloy of titanium and/or zirconium, said method comprising the steps of (a) heat-treating the article formed of titanium, zirconium or alloy of titanium and/or zirconium in an oxidising atmosphere at a temperature in the range of 700 to 1000 °C so as to form an oxide layer on the article; and (b) further heat-treating the article in a vacuum or in a neutral or an inert atmosphere at a temperature in the range of 700 to 1000 °C so as to cause oxygen from the oxide layer to diffuse into the article whereby to produce a sigmoid-shaped hardness profile

3. A method as claimed in claim 2, wherein the oxidising atmosphere contains both oxygen and nitrogen.

4. A method as claimed in claim 1 or 3, wherein the oxidising atmosphere in step (a) is air.

5. A method as claimed in any preceding claim, wherein the time

for heat-treatment in step (a) is from 0.1 to 1 hour.

6. A method as claimed in any preceding claim, wherein the time for heat-treatment in step (a) is from 0.3 to 0.6 hour.

7. A method as claimed in any preceding claim, wherein the heat-treatment in step (a) is effected at atmospheric pressure.

8. A method as claimed in any preceding claim, wherein steps (a) and (b) are repeated at least once.

9. A method as claimed in any preceding claim, wherein the temperature in step (a) is 700 to 900 °C.

10. A method as claimed in claim 9, wherein the temperature in step (a) is 800 to 900 °C.

11. A method as claimed in any preceding claim, wherein the temperature in step (b) is 700 to 900 °C.

12. A method as claimed in claim 11, wherein the temperature in step (b) is 800 to 900°C.

13. A method as claimed in any preceding claim, wherein the heat treatment in step (b) is effected at a pressure of not more than 1.3×10^{-2} Pa (1×10^{-4} Torr).

14. A method as claimed in claim 13, wherein the heat treatment in step (b) is effected at a pressure of about 1.3×10^{-4} Pa (1×10^{-6} Torr).

15. A method as claimed in any preceding claim, wherein the heat

treatment in step (b) is effected for a time in the range of 10 to 30 hours.

16. An article formed of a metal or alloy selected from titanium, zirconium, alloys of titanium and alloys of zirconium, said article having a hardened metallic case, strengthened by diffused oxygen; wherein the article has a sigmoid-shaped hardness profile across said hardened case.

17. An article as claimed in claim 16, wherein the depth of the hardened case is greater than 50 µm.

18. An article as claimed in claim 16, wherein the depth of the hardened case is in the range 200 to 500 µm.

19. An article as claimed in claim 16, 17 or 18, wherein a further layer of low-friction material is provided on top of the hardened case.

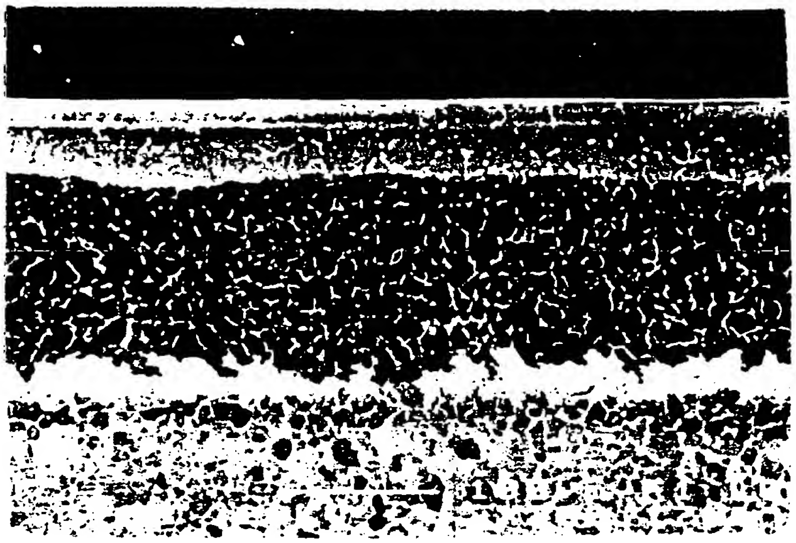


Figure 1

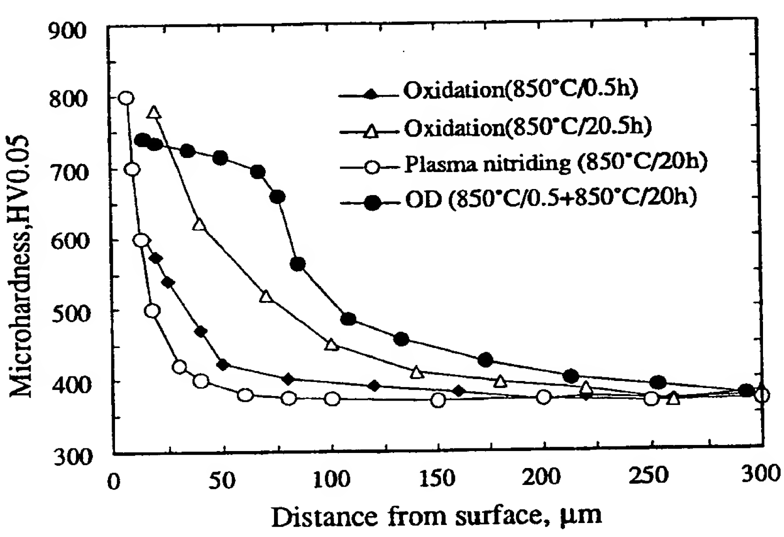


Figure 2

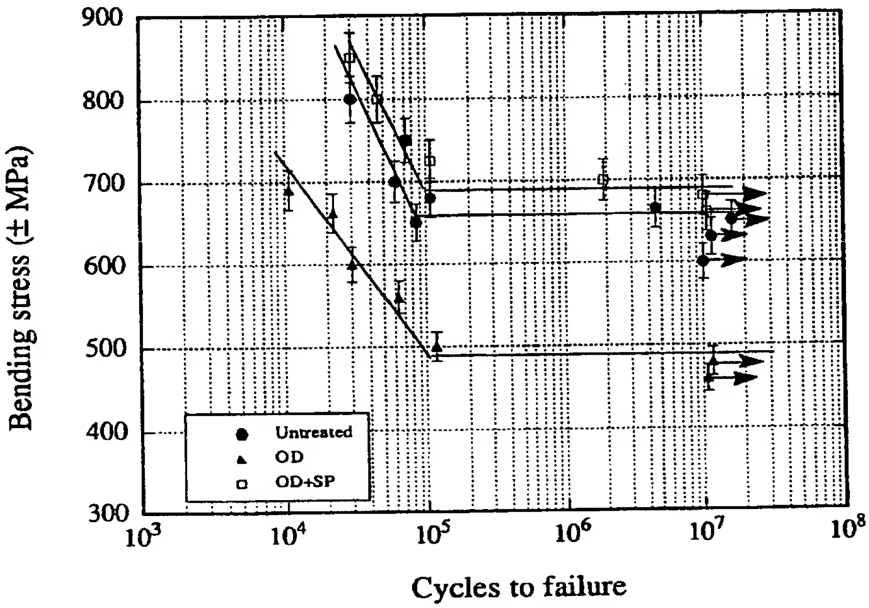

Bending stress (± MPa)
900
800
700
600
500
400
300
10^3
10^4
10^5
10^6
10^7
10^8
Cycles to failure
Untreated
OD
OD+SP

Figure 3

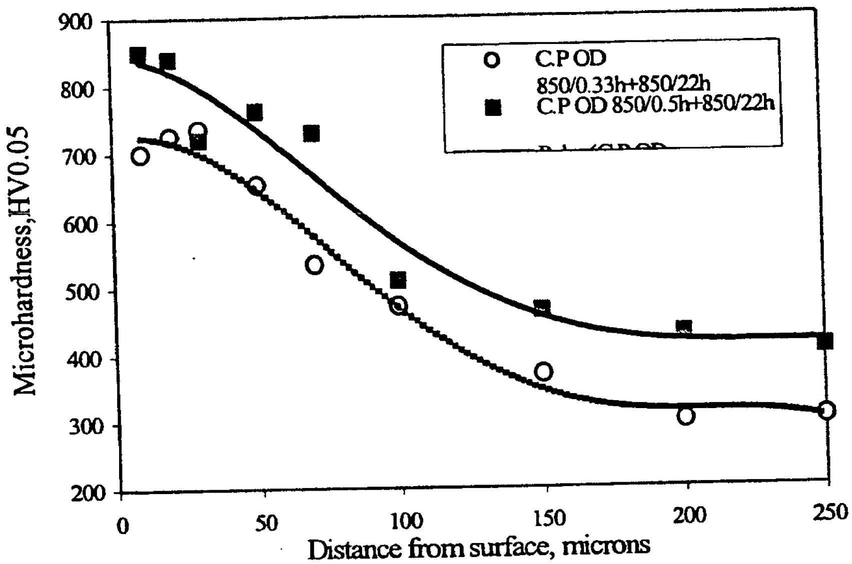


Figure 4

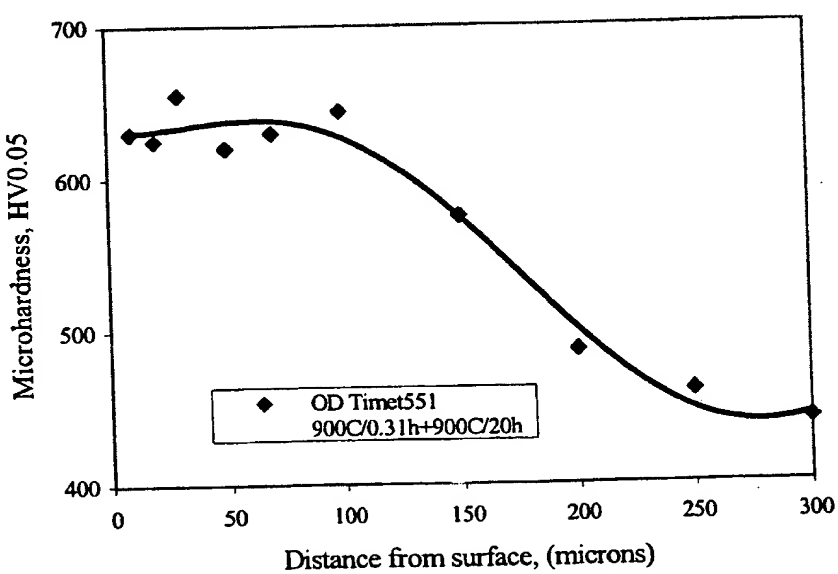


Figure 5

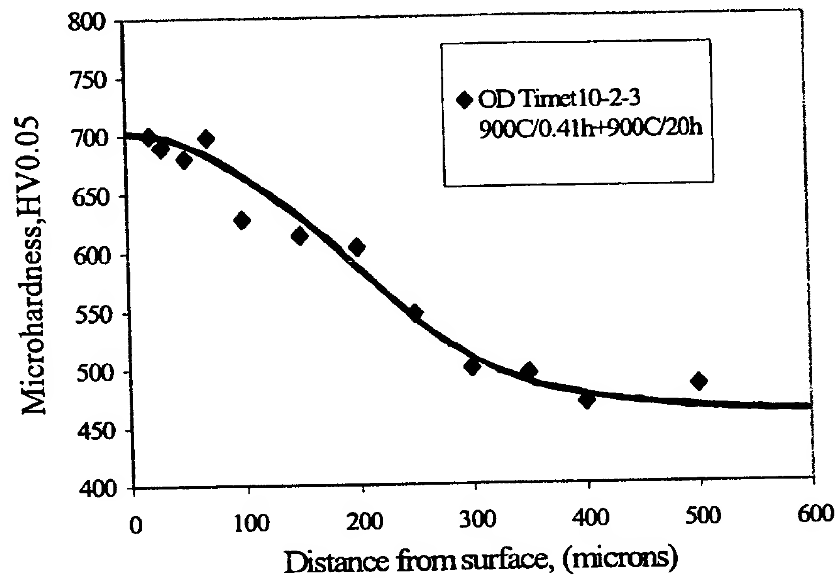

800
750
700
650
600
550
500
450
400
Microhardness,HV0.05
◆ OD Timet10-2-3
900C/0.41h+900C/20h
0
100
200
300
400
500
600
Distance from surface, (microns)

Figure 6